



## A facile approach to prepare self-cross-linkable sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells

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### ABSTRACT

Sulfonated poly(ether ether ketone) containing hydroxyl groups (SPEEK-OH) has been prepared for use as a proton exchange membrane (PEM) by reducing the carbonyl groups on the main chain of the polymers. With the goal of reducing water uptake and methanol permeability, a facile thermal-cross-linking process is used to obtain the cross-linked membranes. The properties of the cross-linked membranes with different cross-linked density are measured and compared with the pristine membrane. Notably, SPEEK-4 with the highest cross-linked density shows a water uptake of 39% and a methanol permeability of  $2.52 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which are much lower than those of the pristine membrane (63.2% and  $5.37 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , respectively). These results indicate that this simple approach is very effective to prepare cross-linked proton exchange membranes for reducing water uptake and methanol permeability.

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### 1. Introduction

In the past few years, direct methanol fuel cells (DMFCs) have received much attention for portable power microelectronics applications because they possess several advantages, including a low operating temperature, easy fuel storage and low explosive characteristics [1,2]. As a key component in this system, proton exchange membrane (PEM) functions as an electrolyte for transferring protons and provides a barrier to the gases or fuel cross-leaks between the electrodes. Up to now, perfluorosulfonic acid membranes, such as Nafion, are commercially used as PEMs because of their excellent chemical resistance, mechanical stability and high proton conductivity [3]. However, some specific limitations exist for Nafion membranes including very high cost, high methanol permeability and loss of the preferable properties at high temperature ( $t > 80^\circ \text{C}$ ) [4]. This stimulated many efforts in developing alternative PEMs for DMFCs.

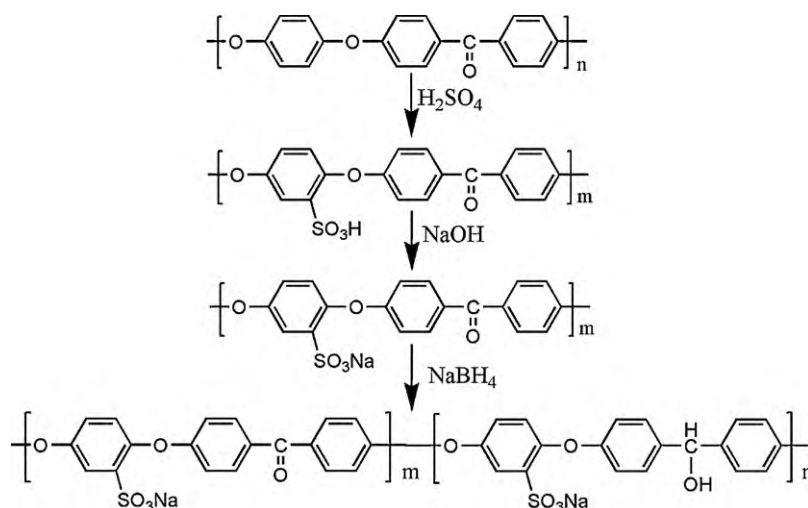
Sulfonated aromatic hydrocarbon polymers, such as SPEEK, have been widely studied as a substitute for Nafion due to their high proton conductivity, excellent mechanical properties and acceptable cost [5–9]. Generally, these sulfonated polymers require high ion exchange capacity (IEC) values to achieve sufficient proton conduc-

tivity. However, high IEC values lead to large dimensional variations and loss of mechanical properties, which render the membranes unsuitable for practical applications in DMFCs. Cross-linking seems to be an effective method to overcome these problems, and cross-linked polymer membranes based on SPEEK polymers had been performed by several groups [10–19]. However, some of these cross-linked membranes suffered from the reduction of the IEC after elimination of sulfonic acid groups, which were involved in the cross-linking reaction, thus giving decreased proton conductivity [15–17]. In our previous work, we prepared SPEEK-PVA cross-linked membranes. Though the cross-linked membranes showed improved mechanical properties and low methanol permeability compared to the pristine membrane, the introduction of cross-linker (PVA) diluted the concentration of sulfonic acid groups, thus decreased proton conductivity [18].

Herein, we report on a facile method to prepare self-cross-linked SPEEK membranes without introducing any cross-linker into the system. The sulfonated poly(ether ether ketone) with hydroxyl groups (SPEEK-OH) was first synthesized according to the method reported by Feng et al. previously [20]. Then cross-linked membranes were obtained by thermal-cross-linking process. The resulting self-cross-linked membranes were investigated as PEMs and compared with the pristine SPEEK membrane. All the results showed that the cross-linking technique was an effective way to overcome the drawbacks of the SPEEK membranes and these self-cross-linked membranes were suitable for DMFC applications.

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**Scheme 1.** Preparation of SPEEK and SPEEK-OH.

## 2. Experimental

### 2.1. Materials

Sodium borohydride ( $\text{NaBH}_4$ ), dimethyl sulfoxide (DMSO), poly(ether ether ketone) (PEEK) and other reagents were commercially available grade and used without further purification.

### 2.2. Characterization

$^1\text{H}$  NMR experiments were carried out on a Bruker 510 spectrometer ( $^1\text{H}$ , 500 MHz) using  $\text{DMSO}-d_6$  as a solvent. The thermal stability was measured using a Pyris 1 TGA (Perkin-Elmer) equipment. All the membranes were heated from  $100^\circ\text{C}$  to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  in  $\text{N}_2$  flow.

### 2.3. Preparation of sulfonated poly(ether ether ketone)

As shown in Scheme 1, SPEEK was obtained through a post-sulfonation process: 10 g PEEK was dissolved in 100 mL sulfuric acid and the solution was then stirred for 4.5 h at  $80^\circ\text{C}$ . The polymer solution was isolated in an excess amount of deionized water and the resulting solid was washed thoroughly with deionized water until the water was neutral. Finally, the product was dried under vacuum at  $80^\circ\text{C}$  for 24 h.

### 2.4. Preparation of sulfonated poly(ether ether ketone) with hydroxyl groups (SPEEK-OH)

SPEEK-OH was prepared through a reduction reaction of carbonyl groups by  $\text{NaBH}_4$ : 4 g SPEEK (in  $\text{Na}^+$ ) was dissolved in 70 mL of dimethyl sulfoxide at  $120^\circ\text{C}$ . 0.2 g  $\text{NaBH}_4$  was added and the mixture was stirred at this temperature for 1–8 h. After cooling to room temperature, the solution was poured into 500 mL of acetone. The resulting solid was then washed with deionized water thoroughly and dried under vacuum at  $60^\circ\text{C}$  for 24 h.

### 2.5. Preparation of pristine membrane and cross-linked membranes

The membranes were prepared using a solution-casting method: 1 g of the polymer was dissolved in 10 mL of dimethyl sulfoxide, and the solution was cast onto a glass plate and dried at  $50^\circ\text{C}$  for 24 h. All the membranes were transformed to their acid forms

by soaking in 1.0 M HCl solution for 24 h. For the cross-linked membranes, the resulting  $\text{H}^+$  form membranes were heated at  $110^\circ\text{C}$  for 6 h under vacuum for forming cross-linking bonds.

### 2.6. Mechanical properties of membranes

The mechanical properties of membranes were measured on a Shimadzu AG-1 1KN equipment. Membrane specimens of  $15\text{ mm} \times 4\text{ mm}$  were placed between the grips of the testing machine at a tensile rate of  $2\text{ mm min}^{-1}$ .

### 2.7. Ion exchange capacity (IEC)

The IEC of membranes was determined by a classical titration method: acid-form membranes were immersed in 2 M NaCl solution for 48 h, and the solution was titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The titrated IEC was obtained from the following formula:

$$\text{IEC} = \frac{\text{Consumed NaOH (mL)} \times \text{molarity of NaOH}}{\text{weight of dried membrane}} (\text{mequiv. g}^{-1}) \quad (1)$$

### 2.8. Water uptake and swelling ratio

The dried square membranes ( $\text{H}^+$  form) were immersed into deionized water at the desired temperature for 24 h. Then the membranes were taken out and wiped with tissue paper quickly. The weight and the length (in plane) were quickly measured. The water uptake and the swelling ratio were calculated by the changes in weight and length between fully hydrated and dry membranes as follows:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the masses of wet and dry membranes,  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the length of wet and dry membranes, respectively.

### 2.9. Proton conductivity

The proton conductivity was measured by a four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287,

Farnborough Hampshire, ONR, UK). The membranes (1 cm × 4 cm) were sandwiched between two pairs of gold-plate electrodes and they were set in a Teflon cell. Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water at desired temperature [21]. The proton conductivity was calculated by the following equation:

$$\sigma = \frac{L}{R \times S} \quad (4)$$

where  $L$  (1 cm) is the distance between the two electrodes,  $R$  is the membrane resistance and  $S$  ( $d \times 1$  cm, where  $d$  is the thickness of membranes) is the cross-sectional area of membranes.

### 2.10. Methanol permeability

A glass diffusion cell was used to measure the methanol permeability as described in the literature [22]. The cell consisted of two reservoirs, which were separated by a membrane. 10 M methanol solution and deionized water were placed on each side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol in water reservoir was determined by using a Shimadzu GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (5)$$

where  $A$  (cm<sup>2</sup>) and  $L$  (cm) are the effective area and the thickness of the membrane, respectively,  $V_B$  (cm<sup>3</sup>) is the volume of diffusion reservoir,  $C_A$  and  $C_B$  (mol L<sup>-1</sup>) are the methanol concentration in methanol reservoir and water reservoir, respectively,  $DK$  is the methanol permeability (cm<sup>2</sup> s<sup>-1</sup>).

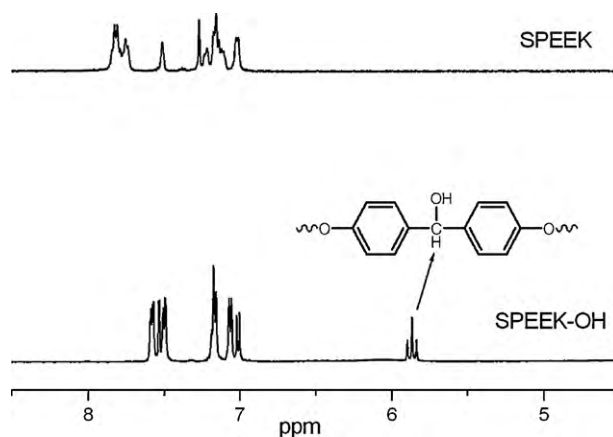
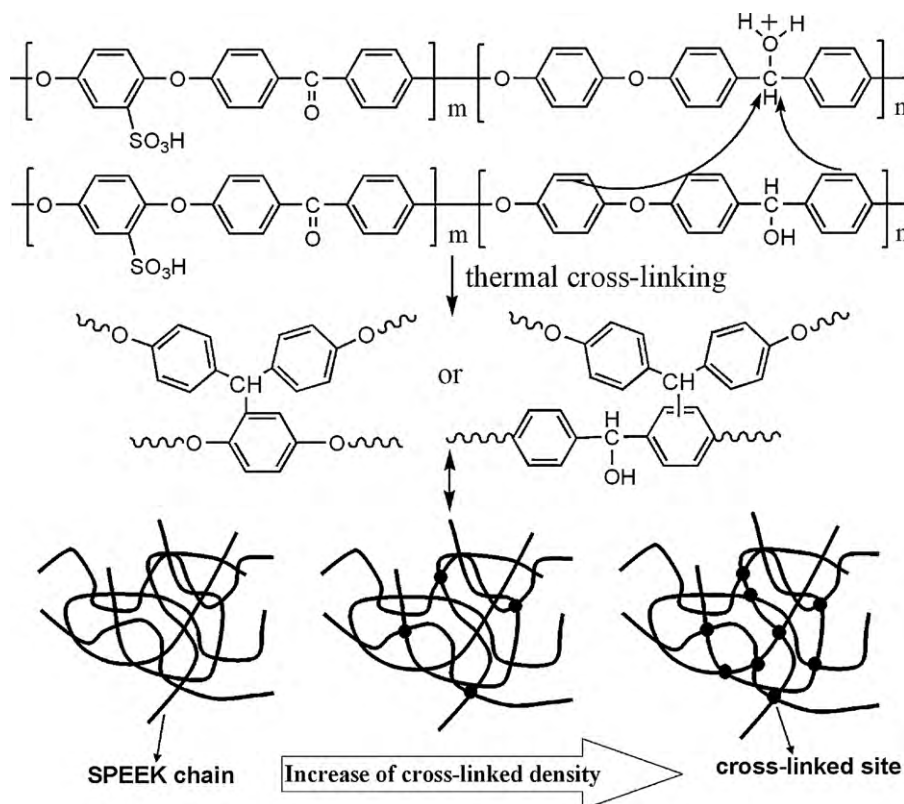


Fig. 1. <sup>1</sup>H NMR spectrum of SPEEK and SPEEK-OH.

## 3. Results and discussion

### 3.1. Preparation of SPEEK-OH and self-cross-linked membranes

Scheme 1 shows the preparation procedure of SPEEK and SPEEK-OH. SPEEK was synthesized through a post-sulfonation process as previously reported by many groups [23]. Parts of the benzophenone moieties in SPEEK were then reduced into the corresponding benzhydrol moieties using NaBH<sub>4</sub> as a reducing agent, and the reductive reaction was confirmed by <sup>1</sup>H NMR spectroscopy. From Fig. 1, the new peak at 5.8 ppm was attributed to the hydrogen of benzhydrol moieties. The degree of hydroxylation was controlled by varying the reduction time (see samples SPEEK-1 to SPEEK-4 in Table 1). A cross-linking reaction was performed via an electrophilic aromatic substitution mechanism under acidic conditions



Scheme 2. Schematic representation of the postulated cross-linked structure.

**Table 1**  
Hydroxylation degree, IEC and gel fraction of membranes.

Polymer membranes	Reduction time (h)	Hydroxylation degree <sup>a</sup> (%)	IEC (mequiv. g <sup>-1</sup> )	Gel fraction <sup>b</sup> (%)
SPEEK	0	0	1.71	0
SPEEK-1	1	24	1.69	31.0
SPEEK-2	2	33	1.67	63.8
SPEEK-3	4	43	1.71	68.6
SPEEK-4	8	69	1.73	76.2

<sup>a</sup> Hydroxylation degree was determined by <sup>1</sup>H NMR.

<sup>b</sup> Gel fraction was obtained from the ratio of the weight of the cross-linked membranes after extraction from DMSO and the initial weight.

(Scheme 2) to obtain cross-linked membranes. As reported by Song et al., the sulfonic acid groups provided acidic protons that activated the benzhydryl groups and made these groups become more electrophilic [10].

### 3.2. Gel fraction of cross-linked membranes

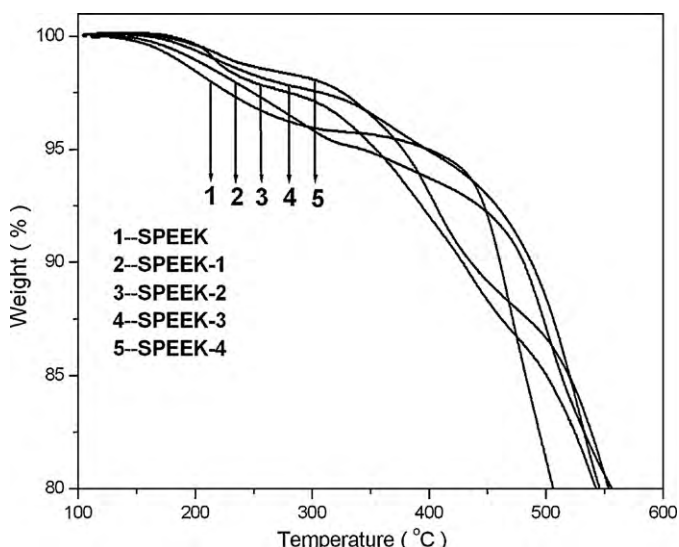
The pristine SPEEK membrane can be easily dissolved in common organic polar solvents, such as DMSO, while the cross-linked membranes cannot be dissolved in this solvent. Gel fraction which can be considered as an indirect measurement of cross-linking density, was obtained from the ratio of the weight of the cross-linked membranes after extraction from DMSO and the initial weight. From Table 1, gel fraction increased with increasing the reduction time, which indicated an increment of cross-linked density.

### 3.3. Thermal stability of membranes

The TGA curves of both pristine SPEEK and cross-linked membranes are shown in Fig. 2. It can be seen that the cross-linked membranes displayed improved thermal stability compared with the pristine SPEEK before 300 °C. The decomposition of main chain of pristine SPEEK occurred around 400 °C, while for the cross-linked membranes, there is an obvious weight loss around 300 °C, which may be due to the decomposition of benzhydryl moieties.

### 3.4. Mechanical properties of the membranes

It is essential for electrolyte membranes to have good mechanical strength to be used in fuel cells. As shown in Table 2, the pristine



**Fig. 2.** TGA curves of SPEEK and cross-linked membranes.

**Table 2**  
Mechanical properties of membranes.

Polymer membranes	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
SPEEK	645.5	31.6	27.5
SPEEK-1	1416.2	51.9	16.3
SPEEK-2	1143.0	47.1	17.6
SPEEK-3	1099.6	52.4	23.4
SPEEK-4	965.6	45.7	19.8

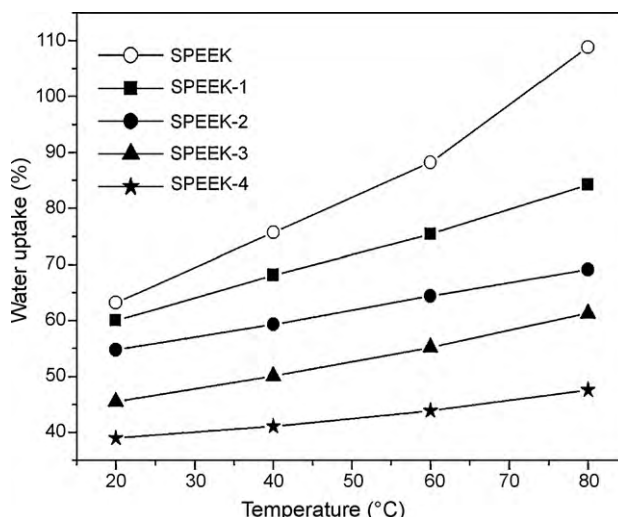
membrane had a Young's modulus of 645.5 MPa, a tensile strength of 31.6 MPa and an elongation at break of 27.5%. All the cross-linked membranes displayed greatly improved Young's modulus and tensile strength which are in the range of 965.6–1416.2 MPa and 45.7–52.4 MPa. However, the elongation at break of the cross-linked membranes was lower than that of the pristine membrane. These results indicate that the cross-linked network structure restricts the motion of the polymer chains resulting in stronger membrane. On the other hand, the cross-linked network structure reduces the flexibility of the membrane [13].

### 3.5. Ion exchange capacity (IEC)

The IEC which is an indication of the density of sulfonic acid groups in membranes was determined by titration. The IEC values of all the membranes are listed in Table 1. It can be seen that cross-linking does not reduce the IEC values because the sulfonic acid groups are not eliminated in the cross-linking reaction. The maintaining IEC is helpful to prepare cross-linked membranes because it is beneficial to high proton conductivity [16].

### 3.6. Water uptake and swelling ratio

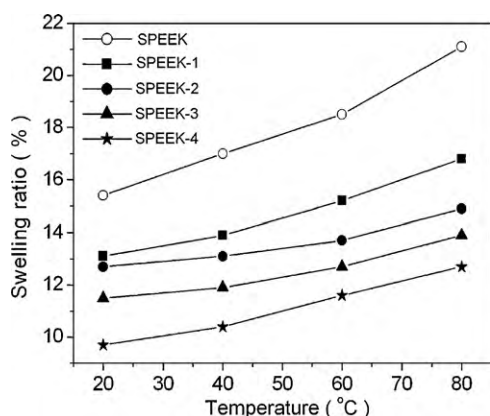
The water uptake of PEMs is very important because it is directly related to the proton conductivity. However, excessive water uptake and high swelling ratio can lead to the loss of mechanical properties and increment of methanol permeability. Generally, the post-sulfonated polymers absorb more water molecules than the pre-sulfonated polymers with similar IEC. As shown in Figs. 3 and 4, the pristine membrane displayed a high water uptake and a swelling ratio of 108% and 21% at 80 °C, respectively. However, the cross-linked membranes exhibited much less water uptake and improved dimensional stability. For example, SPEEK-4 with the highest cross-linked density had the lowest water uptake and



**Fig. 3.** Water uptake of membranes at different temperatures.

**Table 3**  
Water uptake, swelling ratio, proton conductivity and methanol permeability of membranes.

Polymer membranes	Water uptake (%)		Swelling ratio (%)		Proton conductivity ( $\text{S cm}^{-1}$ )		Methanol permeability ( $\text{cm}^2 \text{s}^{-1}$ ) $\times 10^{-7}$
	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C	
SPEEK	63.2	108.8	15.4	21.1	0.013	0.038	5.37
SPEEK-1	60.0	84.2	13.1	16.8	0.010	0.036	4.29
SPEEK-2	54.8	69.1	12.7	14.9	0.0097	0.034	4.05
SPEEK-3	45.5	61.3	11.5	13.9	0.0079	0.031	3.49
SPEEK-4	39.0	47.6	9.7	12.7	0.0073	0.030	2.96

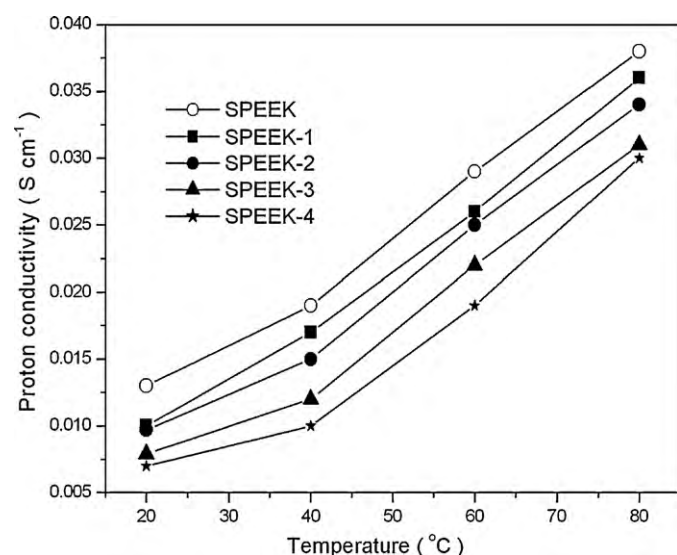


**Fig. 4.** Swelling ratio of membranes at different temperatures.

swelling ratio at 80 °C (47.6% and 12.7%, respectively). From these results, it can be concluded that the cross-linking method in this work is very effective to decrease the water uptake and improve the dimensional stability of the membranes, since cross-linking bonds can hold the polymer chains together to restrict the hydrophilic domains [1].

### 3.7. Proton conductivity and methanol permeability

The proton conductivity of all the membranes at 100% RH was measured and the results are shown in Fig. 5. As seen, the proton conductivity of the membranes increased in proportion to the measuring temperature. The proton conductivity of the pristine membrane was  $0.038 \text{ S cm}^{-1}$  at 80 °C. After cross-linking, the mem-



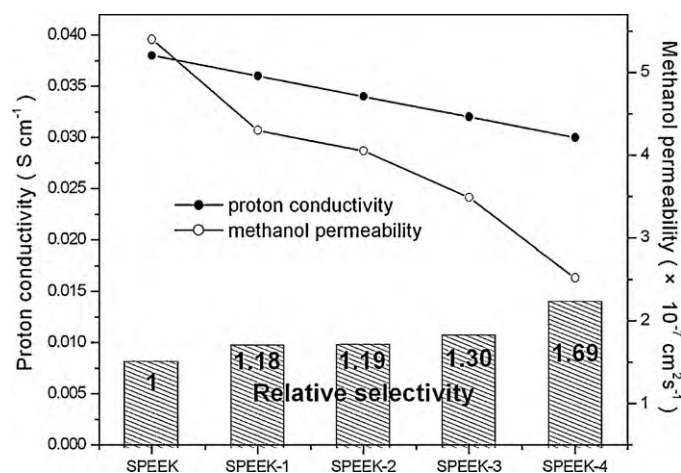
**Fig. 5.** Proton conductivity of membranes at different temperatures.

branes showed slightly low proton conductivity compared to the pristine membrane due to their relatively low water content. Generally, low water content leads to low conductivity due to the diminishment of a hydrophilic, ion conductive network [24]. However, the proton conductivity of all the cross-linked films was still above  $0.03 \text{ S cm}^{-1}$  at 80 °C. Combined with the results of water uptake and swelling ratio, the cross-linking technique used in this work allows the membranes to retain a high level of proton conductivity with greatly improved dimensional stability.

To prevent fuel from penetrating and energy efficiency loss, the proton exchange membranes used in direct methanol fuel cells (DMFCs) should possess well methanol resistance property. One of the drawbacks of highly sulfonated SPEEK is the high methanol permeability. Table 3 shows the methanol permeability of the membranes. The pristine membrane showed a methanol permeability of  $5.37 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , while the cross-linked membranes showed drastically reduced methanol permeability from  $2.52 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  to  $4.29 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . As reported previously, water transportation and methanol permeation take place through the same pathway in the membrane, such as the hydrophilic cluster channels [25]. The cross-linking restricted the hydrophilic domains and suppressed the swelling of the membranes, which resulted in an improved methanol resistance property.

### 3.8. Relative selectivity

The selectivity (the ratio of proton conductivity to methanol permeability) is a common metric for evaluating membrane performance. Fig. 6 shows the relative selectivity of the cross-linked membranes to the pristine membrane. As shown, the proton conductivity displayed a slow reduction with increasing the cross-linked density, while the methanol permeability showed an obvious reduction with the cross-linked density, which resulted in the improved selectivity. SPEEK-4 with the highest cross-linked



**Fig. 6.** The relative selectivity of cross-linked membranes (proton conductivity at 80 °C, methanol permeability at 20 °C).

density had the highest relative selectivity of 1.69. The improved selectivity shows that the cross-linked membranes could be potentially used for DMFC applications.

#### 4. Conclusion

In summary, we reported a facile approach to prepare self-cross-linked SPEEK membranes. The method presented here did not require any cross-linker or catalyst, which avoided an otherwise troublesome preparation process and potential reduction of membrane properties. The resulting cross-linked membranes displayed low water uptake and methanol permeability, while the proton conductivities were comparable to that of the pristine membrane. The high selectivity of the cross-linked membranes indicated that this cross-linking approach was effective in preparing PEMs for DMFCs. Furthermore, this approach is applicable to all the sulfonated poly(aryl ether ketone) materials, which is especially useful for the modification of ketone-containing sulfonated polymers used for PEMs.

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#### References

- [1] M.H. Jeong, K.S. Lee, J.S. Lee, *Macromolecules* 42 (2009) 1652–1658.
- [2] T. Suda, K. Yamazaki, H. Kawakami, *J. Power Sources* 195 (2010) 4641–4646.
- [3] Y. Lin, H.D. Li, C.P. Liu, W. Xing, X.J. Ji, *J. Power Sources* 185 (2008) 904–908.
- [4] Y. Yin, S. Hayashi, O. Yamada, H. Kita, K.I. Okamoto, *Macromol. Rapid Commun.* 26 (2005) 696–700.
- [5] K.S. Lee, M.H. Jeong, J.P. Lee, J.S. Lee, *Macromolecules* 42 (2009) 584–590.
- [6] H. Maab, S.P. Nunes, *J. Power Sources* 195 (2010) 4036–4042.
- [7] K. Miyatake, Y. Chikashige, E. Higuchi, M. Watanabe, *J. Am. Chem. Soc.* 129 (2007) 3879–3887.
- [8] M.M.H. Sadrabadi, E. Dashtimoghadam, K. Sarikhani, F.S. Majedi, G. Khanbabaei, *J. Power Sources* 195 (2010) 2450–2456.
- [9] J.H. Pang, H.B. Zhang, X.F. Li, D.F. Ren, Z.H. Jiang, *Macromol. Rapid Commun.* 28 (2007) 2332–2338.
- [10] H. Song, S.C. Lee, H.Y. Heo, D.I. Kim, D.H. Lee, J.H. Lee, J.Y. Chang, *J. Polym. Sci.: Part A: Polym. Chem.* 46 (2008) 5850–5858.
- [11] S. Yu, B.C. Benicewicz, *Macromolecules* 42 (2009) 8640–8648.
- [12] J.C. Tsai, C.K. Lin, J.F. Kuo, C.Y. Chen, *J. Power Sources* 195 (2010) 4072–4079.
- [13] D.S. Phu, C.H. Lee, C.H. Park, S.Y. Lee, Y.M. Lee, *Macromol. Rapid Commun.* 30 (2009) 64–68.
- [14] Z.T. Wang, D.D. Jiang, C.A. Wilkie, J.W. Gilman, *Polym. Degrad. Stabil.* 66 (1999) 373–378.
- [15] H. Luo, G. Vaivars, M. Mathe, *Int. J. Hydrogen Energy* 34 (2009) 8616–8621.
- [16] V.R. Hande, S. Rao, S.K. Rath, A. Thakur, M. Patri, *J. Membr. Sci.* 322 (2008) 67–73.
- [17] N. Xu, X. Guo, J. Fang, J. Yin, M. Yuan, B. Chen, *Fuel Cells* 4 (2009) 363–371.
- [18] C.J. Zhao, H.D. Lin, H. Na, *Int. J. Hydrogen Energy* 35 (2010) 2176–2182.
- [19] S.L. Zhong, C.G. Liu, H. Na, *J. Membr. Sci.* 326 (2009) 400–407.
- [20] S.G. Feng, Y.M. Shang, Y.W. Wang, G.S. Liu, X.F. Xie, W.Q. Dong, J.M. Xu, V.K. Mathur, *J. Membr. Sci.* 352 (2010) 14–21.
- [21] Y. Zhang, Z.M. Cui, C.J. Zhao, K. Shao, H.T. Li, T.Z. Fu, H. Na, W. Xing, *J. Power Sources* 191 (2009) 253–258.
- [22] H.T. Li, Z.M. Cui, C.J. Zhao, J. Wu, T.Z. Fu, Y. Zhang, K. Shao, H.Q. Zhang, H. Na, W. Xing, *J. Membr. Sci.* 343 (2009) 164–170.
- [23] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *J. Membr. Sci.* 173 (2000) 17–34.
- [24] P.D. Beattie, F.P. Orfino, V.I. Basura, K. Zychowska, J. Ding, C.J. Chuy, *Electroanal. Chem.* 503 (2001) 45–56.
- [25] C.S. Ma, L. Zhang, S. Mukerjee, D. Ofer, B. Nair, *J. Membr. Sci.* 219 (2003) 123–136.